

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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THE DIRECT PRODUCTION OF A LOW POUR POINT HIGH GRAVITY SHALE OIL

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The production of shale oil by an in situ process has been long recognized as an important step in the potential utilization of the tremendous Green River Oil Shale reserves in the western United States. For the past several years the Equity Oil Company has sponsored a research project in the Fuels Engineering Department of the University of Utah to test a concept of the late Mr. J. L. Dougan that the energy required to heat the rock and convert the kerogen to a mobile oil could be provided by heated natural gas. The hydrocarbons in the natural gas would serve as a compatible solvent for the oil produced and would penetrate the pores and fissures produced as the converted kerogen moved out of its original sites due to its thermal expansion and volatility. The temperature of the heated natural gas could be high enough to produce the desired kerogen decomposition but low enough to minimize endothermal decomposition of the carbonate minerals of the marlstone matrix and the fusion of these minerals which occurs in combustion type, high temperature processes.

The laboratory experiments confirmed the concept and gave the following results.

Natural gas is a suitable heating medium to effect the desired kerogen breakdown with the production of a low pour point, high API gravity crude oil.

Table 1 lists the operating temperatures, pressures and run durations for a series of typical experiments together with the oil yield and properties. Percent of Fischer Assay yield as determined on the same core samples by the Bureau of Mines at Laramie, Wyoming, are also indicated.

TABLE 1
EFFECT OF TEMPERATURE ON OIL YIELD

Test	Temperature	Pressure	Duration	Oil-Weight Percent		U. of U.% of
				U. of U.	Fischer Assay	Fischer Assay
D-4	331°C 628°F	atm	550 hrs	4.0	11.9	33.6
D-5	347 657	atm	425	4.8	11.9	40.4
D-19	353 667	atm	159	4.3	11.0	39.1
D-7	364 687	atm	312	6.0	11.4	52.6
D-22	395 743	atm	71	7.6	10.6	71.6
D-16	399 750	atm	86.5	8.0	11.0	72.8
D-17	420 788	atm	38.0	8.8	11.0	80.0
D-10	427 801	atm	37.5	8.9	11.4	78.1
D-14	427 801	1000 psig	14.7	8.6	11.8	72.9
D-1	500 932	atm	13.5	7.6	8.2	92.6

An excellent indicator for the beginning of kerogen decomposition is the appearance in the product gases of hydrogen sulfide. Figure 1 shows the comparative mass spectrometer peak heights of the $m/e = 34$ (H_2S) for a typical run.

Superimposed on the same temperature plot in the figure is a differential weight loss curve from an oil shale decomposition study by Allred. (1) The correspondence between the hydrogen sulfide evolution and the total product evolution during pyrolysis of the kerogen is most striking. Hydrogen sulfide evolution is a good indicator of the total decomposition process.

Figure 2 illustrates the results of a typical run in which the volume of gas produced during a run is the time dependent parameter. The liquid products from these runs were condensed in a freeze out trap cooled by dry ice in acetone. Weighed samples of the oil shale cores from the Piceance Creek Basin in the Green River Formation were the raw materials in both static and

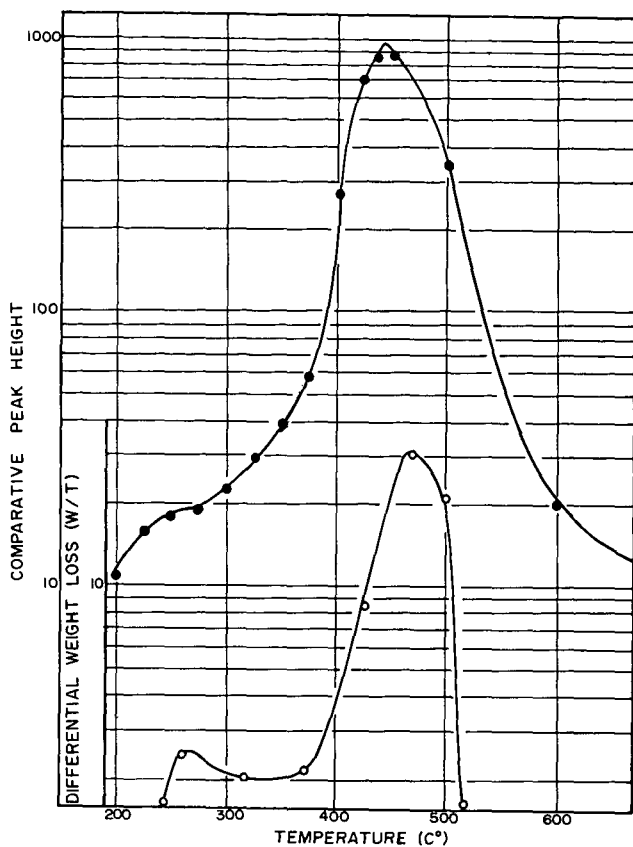
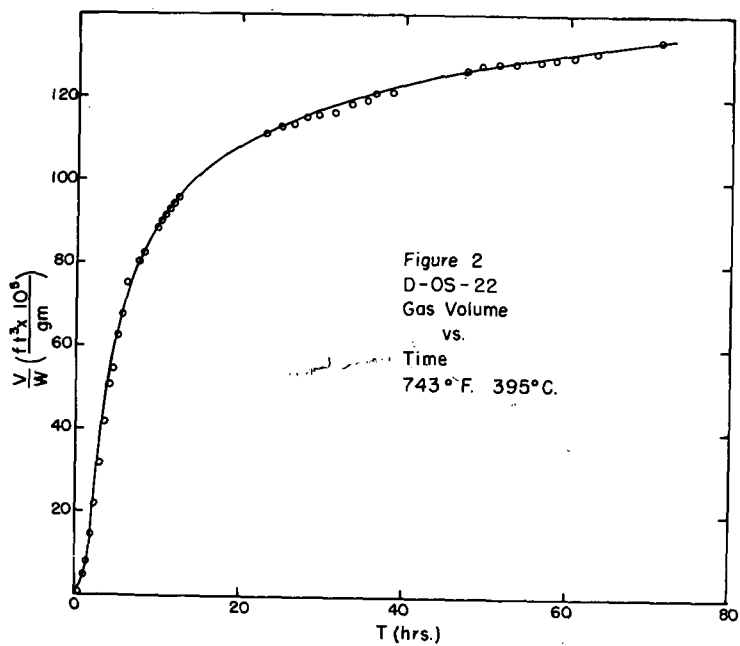


Figure 1. H₂S production (●) and oil production (○) at increasing temperatures.



flow runs. The data obtained on each run included initial and final weights of the oil shale, weight and volume of oil and water and the volume of gas produced. Material balances and product yields were determined for each run.

From the series of gas evolution--time curves at temperatures from 331°C to 427°C the following data can be obtained.

The heat of activation for initial product evolution is 26.7 kcal. During the long term, slower, continuing product evolution an activation energy of 20.5 kcal is calculated. At each temperature oil continues to be evolved at essentially constant rates over periods of up to 550 hours (Figure 3).

Typical analyses of the gases produced from non-flow tests are shown in Table 2 together with the volume of non-condensable gases per gram of original shale.

Data relating to the oil quality as a function of conversion temperature are shown in Table 3.

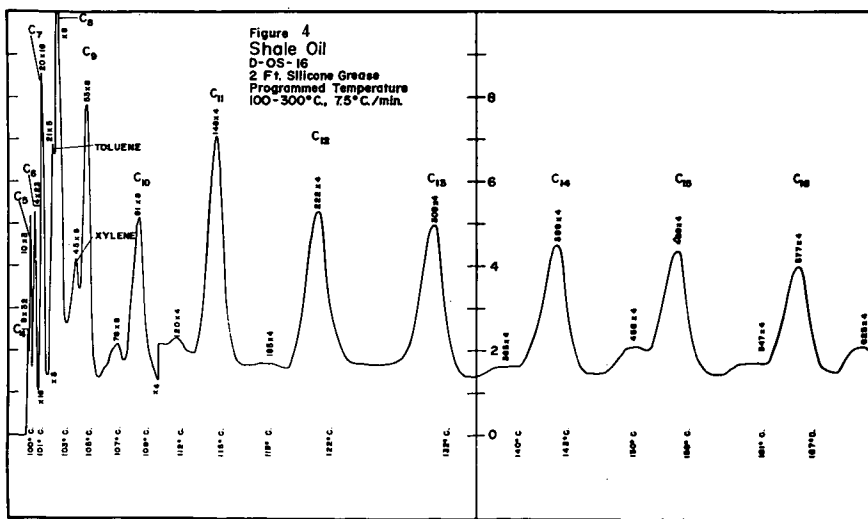
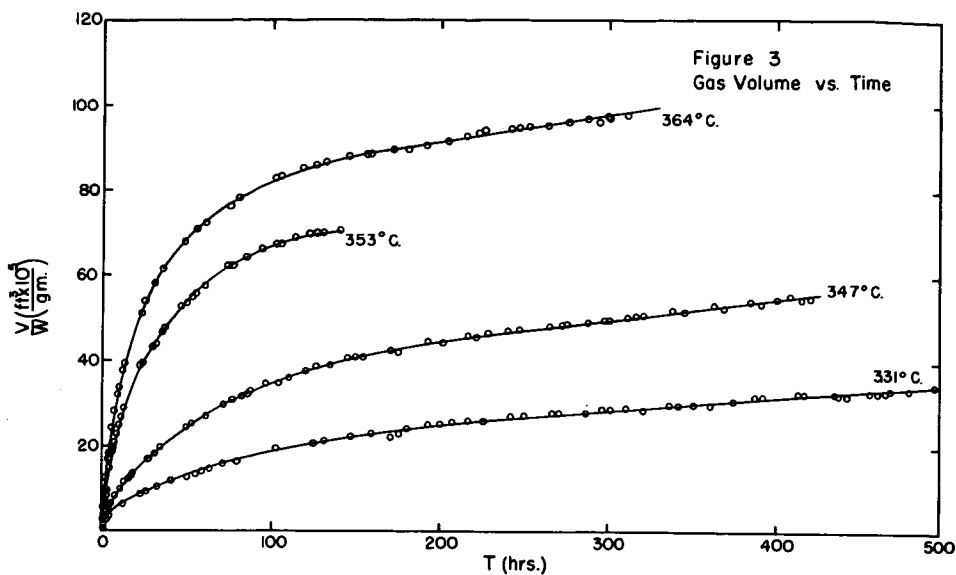
TABLE 2
TEMPERATURE EFFECT ON GAS YIELD AND PRODUCT GAS ANALYSIS

Temperature	Gas Evolved ft ³ x 10 ⁵ /gm	%CO ₂	%CH ₄	%C ₂ H ₆	%C ₃ H ₈	%H ₂ S	%H ₂ +others
170°C	3.21	.27					
300	1.88	30.5	43.6	2.09	3.55		20.3
350	1.7	18.7	15.2	16.3	2.85	.44	46.5
380	2.64	3.8	13.1	4.02	3.40	.90	74.8
404	3.21	3.5	19.2	6.44	4.54	.61	65.7
444	6.61	9.6	28.1	6.92	3.04	.29	52.0
485	6.79	26.7	21.2	1.44	.75		49.9
500	3.58	41.0	9.94	.85	.90		48.2
525	10.7	69.0	4.23	.33			26.4
552	33.4	89.6	2.91				7.5
575	39.6	77.5	1.34				21.2
590	9.25	99.6	.37				

TABLE 3
EFFECT OF TEMPERATURE ON OIL QUALITY

Test	Temperature	Specific Gravity	API Gravity	Pour Point	Fischer Assay Specific Gravity
D-4	628°F 331°C	.822 gm/cm ³	40.7	-40°C	.911 gm/cm ³
D-5	657 347	.823	40.5	-45	.911
D-19	667 353	.828	39.4	-23	.914
D-7	687 364	.817	41.6	-18	.912
D-22	743 395	.838	37.4	-20	.910
D-16	750 399	.828	39.4	-23	.914
D-17	788 420	.832	38.6	-20	.914
D-10	801 427	.888	27.7	-5	.912
D-14	800 427(1000psig)	.814	42.3	-22	.903
D-1	932 500	.852	34.6	10	.907
D-2	968 520	.859	33.5	0	.907

One explanation of the difference in the quality of the oil with temperature is that cracking the kerogen at minimum decomposition temperatures produces relatively low molecular weight primary product molecules of sufficient stability that they do not undergo polymerization. At higher temperatures secondary cracking and polymerization reactions occur producing the usual high pour point, low gravity material. The same difference has long been known between coal oil, a low temperature distillate, and coal tar, a high temperature product. In Table 3 it is noted that there is a general correlation between the temperature of the experiment and the API gravity and the pour point of the oil produced. At temperatures below 420°C, at atmospheric pressure the oils varied from 37 to 41 degrees API and were liquids to below -18°C. Oils produced at higher temperatures were lower in gravity and had a higher pour point.



The oil produced in test run D-14 at 1000 psig and 427°C had an API gravity and pour point characteristic of oils produced at lower temperatures.

The specific gravity of the oil produced in the Fischer Assay of the same samples is given for comparison.

For comparative purposes ultimate analyses of typical high temperature shale oils from approximately the same stratigraphic horizon and from a Pumpherston retort sample are given in Table 4. Most significant here are the lower nitrogen content and the higher hydrogen content of the low temperature product.

TABLE 4
COMPARISON OF U. OF U. SHALE OIL WITH SHALE OILS FROM OTHER SOURCES

Shale Oil	Retort	%C	%H	%N	%S	%O	C/H
Colorado	U. of U.	83.9	12.5	.65	1.15	1.84	6.71
Colorado	N-T-U	84.5	11.3	1.77	.75	1.63	7.48
Kimmeridge, England	Pumpherston	80.9	8.6	1.4	6.5	2.6	9.4

Table 5 gives the ultimate analyses and C/H ratio for a series of oils produced in our laboratory at 300 psi but at increasing temperatures from 370°C to 493°C.

Significantly the nitrogen content was lower in the low temperature samples. The percentages of nitrogen and sulfur appeared to go through maxima. The oxygen content was fairly constant above temperatures of 425°C.

The C/H ratio was lowest in the oils produced at the lower temperatures.

TABLE 5
EFFECT OF TEMPERATURE ON SHALE OIL
ULTIMATE ANALYSES FROM A FLOW STUDY AT 300 PSIG.

Sample	Temp. °C	%C	%H	%N	%S	%O	C/H
HP-14-2	370	83.9	12.5	.65	1.15	1.84	6.71
HP-14-3	400	84.0	12.6	.6	1.16	1.36	6.66
HP-14-4	425	84.8	12.3	.83	1.31	1.08	6.89
HP-14-5	430	84.6	12.6	.91	1.61	1.24	6.71
HP-14-6	450	85.0	12.2	1.11	1.30	1.01	6.96
HP-14-7	480	84.5	12.0	1.46	1.27	1.11	7.04
HP-14-8	485	84.5	12.0	1.41	1.04	1.11	7.04
HP-14-9	490	84.6	11.9	1.01	1.24	1.07	7.11
HP-14-10	493	84.2	11.8	1.08	.96	1.11	7.14

Microscopic examination of the shale residue shows interesting results. As the kerogen decomposes and volatilizes it leaves voids in the otherwise unaltered rock. These voids provide an interconnecting network and an internal porosity in the previously impermeable shale.

Measured values of porosity and permeability before and after thermal treatment at 480°C are shown in Table 6. These results confirm the important findings of Thomas (2) who heated shale plugs ingeniously confined at pressures approximating those to be encountered in situ heating at depth. He reported comparably high porosities but lower permeability. Our experiments in the laboratory were performed at gas pressures up to 400 psi but without physically confining mechanical pressure.

When Green River oil shale (marlstone) is heated to temperatures used in the Fischer Assay (or other conventional retorting processes) the constituent mineral carbonates decompose. The spent shale is ordinarily partially fused in the process. The carbonate decomposition is endothermic and wasteful of thermal energy. Also the resulting mass is not permeable or porous. Problems resulting from these phenomena have been serious in attempts in situ firing experiments.

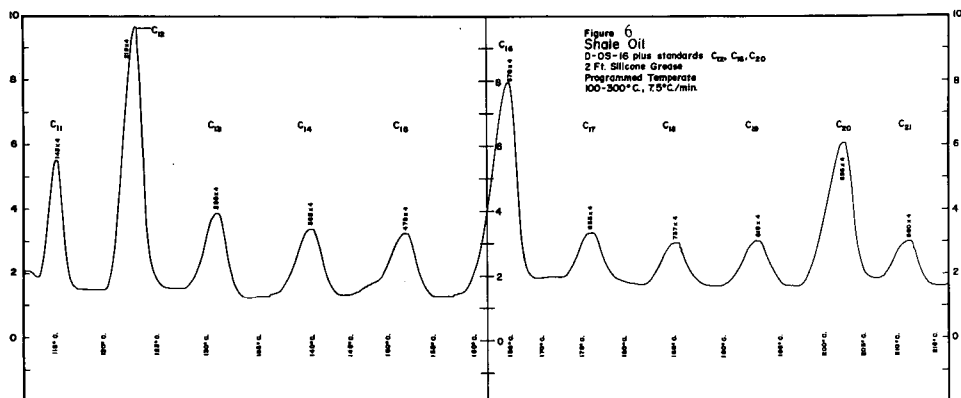
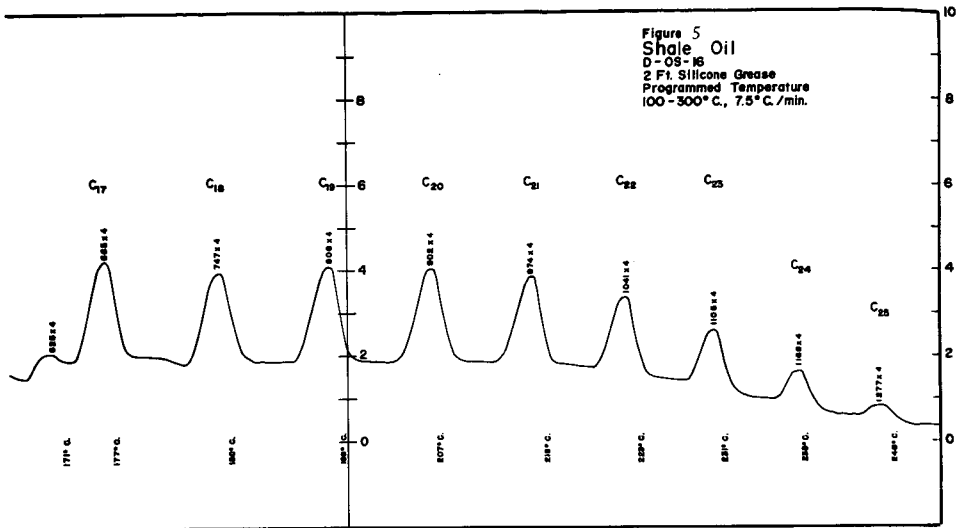


TABLE 6
POROSITY AND PERMEABILITY OF OIL SHALE

Test	Sample Description	Temp. °C	Pressure psig	Permeability Millidarcys		Porosity %
				Horizontal	Vertical	
	Raw Shale			0.0	0.0	0.8
HP-8	Spent Shale Top of Reactor	480	300	125	4.7	44.7
HP-6	Spent Shale Top of Reactor	485	300	5.7	4.3	30.6
	Bottom of Reactor	485	300	14	2.8	41.5

Figures 4 and 5 show the results of a chromatographic column separation of the components of the oil. An F and M model 720 temperature programmed chromatograph was used. The two foot silicone grease column was used. The heating rate was 7.5°C per minute. The temperature range was from 100°C to 300°C. The probable components in the oil are noted on each peak. Normal paraffin hydrocarbons from C₄ to C₂₅ were identified. No paraffins larger than C₂₅ were detected.

To confirm the identity of several components a sample of the oil was spiked with pure samples of normal, C₁₀, C₁₂, C₁₆, and C₂₀. Figure 6 shows the chromatographic analysis record of the spiked sample. The peaks assumed to be C₁₀, C₁₂, C₁₆ and C₂₀ are each increased relative to adjacent peaks. No broadening or doubling of the peaks is noted confirming the identity assignment.

The heating value of three of the shale oils are given in Table 7. They vary from 18,270 to 19,090 Btu per pound.

TABLE 7
HEATING VALUE OF SHALE OILS

Test	Pressure psig	Oil Heating Value Btu/lb
HP	300	18,270
HP	300	18,450
D-7	Atmos.	19,090

In Summary - Green River Oil Shale can be heated by natural gas to temperatures below the mineral carbonate decomposition temperature with the production of a 40°API, low pour point shale oil in approximately 2/3 Fischer Assay yield. The nitrogen content of the oil is one-third to one-half the content of Fischer Assay oil from the same stratum of shale. Hydrogen sulfide evolution provides a convenient indicator of the kerogen decomposition.

The conversion of the kerogen in the shale to oil and its distillation and mechanical removal from the shale by the hot natural gas produces a porous structure which allows the process to continue through the formerly non-porous, impermeable solid oil shale.

The process has been applied in a field test in the Piceance Creek Basin in Colorado and has produced shale oil of the same quality as that produced in the laboratory.

LITERATURE CITED

- (1) Allred, V. Dean, and Nielson, G. J., "Counter Current Combustion - A Process for Retorting Oil Shale," 48th National Meeting of AIChE., August 26-29, 1962.
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